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Evidence for Carbon−Sulfur Bond Cleavage in Spontaneously Adsorbed Organosulfide-Based Monolayers at Gold

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We have recently described several aspects of the electrode reactions of monolayers formed from alkanethiols[1] and dialkyl disulfides[2] at gold.[3] Our results have shown that these monolayers can be desorbed in alkaline solution via reaction 1.[4]

$$\mathrm{RS{-}Au} + e^- \rightarrow \mathrm{RS}^- + \mathrm{Au} \qquad (1)$$

Implicit in reaction 1 is that either the S−H or S−S bond of the adsorbate precursor is cleaved as a consequence of monolayer formation.[5] Upon extending these studies to related systems, we have discovered that the formation of monolayers from organosulfides at gold[6] is also a dissociative chemisorption process. This previously undetected process results in S−C cleavage in one of the organosulfide side arms, yielding structures tethered to gold like those from alkanethiols and dialkyl disulfides. The following discusses the findings and implications of two sets of electrochemical and surface characterization studies (viz., X-ray photoelectron (XPS) and infrared reflection (IRS) spectroscopies) that are the basis of our conclusion.

The first set of studies characterized monolayers formed at mica-supported Au(111) from dilute (0.1−1 mM) ethanolic solutions of butanethiol (BT/Au; purity, 99.4%) and butyl sulfide (BS/Au; purity, 97.9%).[7] Figure 1A presents the current−potential ($i-E$) curves from linear voltage sweep experiments. The cathodic wave at BT/Au reflects reaction 1[1a,8] and has a peak potential (E_p) at −0.77 V vs the Ag/AgCl (saturated KCl) electrode. After accounting for roughness,[4,9] the charge under the wave (Q_d) equals 75 μC/cm^2, which translates to a surface coverage in reasonable agreement with that expected for this adsorbate−substrate combination.[1,10] Sample-to-sample variabilities in Q_d are ±10%. Importantly, the wave at BS/Au (E_p = −0.78 V, Q_d = 70 μC/cm^2) is indistinguishable from that at BT/Au (E_p = −0.77 V, Q_d = 75 μC/cm^2). The similarity in the E_p values argues that the interaction between sulfur and gold is the same for both types of precursors, whereas the similarity in the Q_d values points to comparable surface coverages. These findings argue strongly that the interfacial structures at BS/Au and BT/Au are the same.

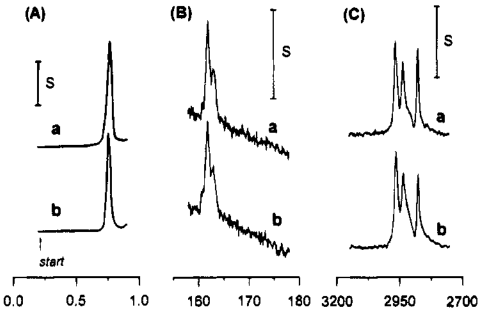

Figure 1. Linear sweep voltammetric curves (A: s = 30 μA-cm^{-2} (geometric area); scan rate, 50 mV/s; supporting electrolyte, 0.5 M KOH; reference electrode, Ag/AgCl(saturated KCl)), XPS spectra (B: s = 5000 counts), and IRS spectra (C: $s = 5.0 \times 10^{-4}$ absorbance units) for monolayers from butanethiol (a) and butyl sulfide (b).

The XPS spectra in the S(2p) region and IRS spectra in the C−H stretching region in Figure 1 provide additional support for the structural similarity at BT/Au and BS/Au.[7] The intensities and positions of the bands in the two types of spectra at both samples have a close correspondence.[11] On the basis of the structural details probed by each technique, the similarities in the XPS data support the comparability of the interaction between sulfur and gold in both systems, whereas the similarities in the IRS data are indicative of a comparable alkyl chain structure.[12,13] For all of the above similarities to exist, it follows that the formation of a monolayer from BS must then result in S−C cleavage in one of the side chains of the symmetric alkyl sulfide.

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[1] (a) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335−59. (b) Walczak, M. M.; Popenoe, D. D.; Deinhammer, R. S.; Lamp, B. D.; Chung, C.; Porter, M. D. *Langmuir* **1991**, *7*, 2687−93. (c) Weisshaar, D. E.; Lamp, B. D.; Porter, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5860−2. (d) Weisshaar, D. E.; Walczak, M. M.; Porter, M. D. *Langmuir* **1993**, *9*, 323−9.

[2] Lamp, B. D.; Porter, M. D. In preparation.

[3] See: (a) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437−63. (b) Soriaga, M. P. *Prog. Surf. Sci.* **1992**, *39*, 326−443. (c) Salaita, G. N.; Hubbard, A. T. In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; John Wiley & Sons, Inc.: New York, 1992; pp 49−118 and references therein.

[4] Recent reports (Majda, M. In *Interfacial Design and Chemical Sensing*; Mallouk, T., Harrison, J., Eds.; ACS Symposium Series 561; American Chemical Society: Washington, DC, 1994; pp 135−44. Schneider, T. W.; Buttry, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 12391−7) have considered reaction 1 as a partial electron transfer process, suggesting that the current required to charge a bare gold surface after desorption is a large portion of Q_d. These studies were, however, conducted for systems either prepared or characterized differently than herein, which may account for the reported differences (also see: Lösch, R.; Stratmann, M.; Viefhaus, H. *Electrochim. Acta* **1994**, *8/9*, 1215−21). We further note that, in 0.5 M KOH, at most 18 μC/cm^2 is required to charge the bare gold surface (J. Zak, N. J. Simmons, M. D. Porter, in preparation), which, along with the ±10% variability in surface roughness, must be considered when analyzing these data. Our desorption modeling studies (C. J. Zhong and M. D. Porter, in preparation) support our analysis.

[5] Several recent vibrational spectroscopic studies support the details embodied in reaction 1. (a) Carron, K. T.; Hurley, G. *J. Phys. Chem.* **1991**, *95*, 9979−84. (b) Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 8284−93. (c) Gui, J. Y.; Stern, D. A; Frank, D. G.; Lu, F.; Zapien, D. C.; Hubbard, A. T. *Langmuir* **1991**, *7*, 955−63. (d) Szafranski, C. A.; Tanner, W.; Laibinis, P. E.; Garrell, R. L. Submitted to *Langmuir* and references therein.

[6] (a) Li, T. T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 6107−8. (b) Troughton, E. B.; Bain, C. D.; Whitesides, G. W.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* **1988**, *4*, 365−85. (c) Steinberg, S.; Tor, Y.; Sabatani, E.; Rubinstein, I. *J. Am. Chem. Soc.* **1991**, *113*, 5176−82. (d) Zhang, M.; Anderson, M. R. *Langmuir* **1994**, *10*, 2807−13.

[7] Preparation and characterization details are given in ref 1. Material purity data are from chromatographic assays by the vendor (Aldrich).

[8] Desorption at rougher gold surfaces exhibits multiple waves, which we attribute to a greater number of atomic steps (M. M. Walczak, C. A. Alves, B. D. Lamp, M. D. Porter, in preparation).

[9] Q_d values were determined using a straight capacitive-baseline approximation and a surface roughness factor of 1.1.[1] At short chain monolayers, additional wave(s) are often found at more negative potentials, which we attribute to a sulfur/polysulfur species arising from cleavage of both S−C bonds. The data herein are for samples where this complication was insignificant. Evidence for S−C cleavage at monolayers from mercaptoethanol is presented in ref 1d.

[10] According to the $(\sqrt{3} \times \sqrt{3})R30°$ packing structure of alkanethiolates at Au(111) (Chidsey, C. E. D.; Liu, G.-Y.; Rowntree, P.; Scoles, G. J. L. *J. Chem. Phys.* **1989**, *91*, 4421), a coverage of 7.6×10^{-10} mol/cm^2 is expected for a densely packed monolayer. Other adlayer arrangements have been observed (see, for example: Poirier, G. E.; Tarlov, M. J. *Langmuir* **1994**, *10*, 2853−6), but with similar packing densities.

[11] (a) Lindberg, B. J.; Hamrin, K.; Johansson, G.; Gelius, U.; Fahlman, A.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *1*, 286−98. (b) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 733−40. (c) Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1993**, *9*, 1766−70.

[12] (a) The aliphatic C−H stretches are observed at 2966, 2935, and 2877 cm^{-1} at BS/Au, and at 2965, 2935, and 2877 cm^{-1} at BT/Au (see ref 3a and references therein for assignments). (b) The XPS spectra show $S(2p_{3/2})$ peaks at 161.9 (BS/Au) and 162.0 (BT/Au) eV, with the $S(2p_{1/2})$ peaks ~1.2 eV higher than the corresponding $S(2p_{3/2})$ peaks. Both features are ~1 eV lower than their adsorbate precursors.[11a]

[13] The slight differences in the two spectra (Figure 1C) suggest a subtle difference in the packing density of the alkyl chains, as discussed previously.[6]

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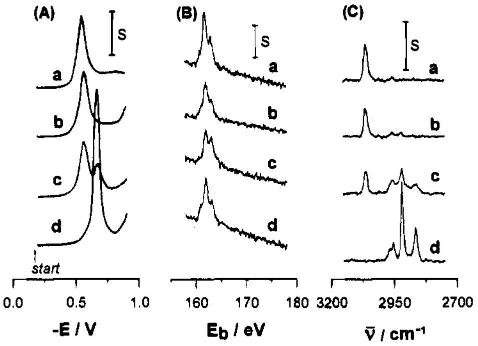

Figure 2. Linear sweep voltammetric curves (A: $s = 15\ \mu$A-cm^{-2} (geometric area)), XPS spectra (B: $s = 5000$ counts), and IRS spectra (C: $s = 5.0 \times 10^{-4}$ absorbance units) for monolayers from thiophenol (a), phenyl sulfide (b), methyl phenyl sulfide (c), and ethanethiol (d). All conditions are the same as in Figure 1.

The second set of experiments compared the monolayers formed from an asymmetric aryl sulfide, ethyl phenyl sulfide (PES; purity, 99.9%), and a symmetric aryl sulfide, phenyl sulfide (PS; purity, 99.9%),[7] with those from thiophenol (TP; purity, 99.7%) and ethanethiol (ET; purity, 99.9%). As Figure 2A shows, the $i-E$ curves at TP/Au, ET/Au, and PS/Au each contain a single desorption wave, with respective E_p and Q_d values[14] of -0.57 V and 52 μC/cm^2, -0.68 V and 87 μC/cm^2, and -0.57 V and 52 μC/cm^2. In contrast, two waves are evident at PES/Au; the E_p and Q_d values are -0.57 V and 34 μC/cm^2 for the more positive wave and -0.67 V and 23 μC/cm^2 for the more negative wave.[15] The similarities in the E_p and Q_d values at TP/Au and PS/Au are consistent with the observations and subsequent interpretation of the electrochemical data at BT/Au and BS/Au. That is, the sulfur–gold interactions at TP/Au and PS/Au are effectively indistinguishable. More importantly, the position of the more positive wave at PES/Au is the same as at TP/Au and PS/Au, and the position of the more negative wave is the same as at ET/Au. The electrochemical data at PES/Au are therefore diagnostic of a monolayer composed of two chemically distinct gold-bound thiolates. On the basis of the structure of the adsorbate precursor, the presence of both types of adsorbates can arise only from S–C cleavage in the side arms of the asymmetric organosulfide. Thus, cleavage at the phenyl side arm of PES yields a gold-bound ethanethiolate species, whereas a gold-bound phenyl thiolate species results from cleavage at the ethyl side arm.

Results of XPS and IRS characterizations[16] of the above four samples (Figure 2B,C) support our interpretation. Following the discussion of Figure 1B, the general comparability of the XPS data fits with the proposed similarity of the interactions between sulfur and gold of each system.[16a] Additionally, the presence of bands attributable only to aryl C–H stretches at TP/Au and PS/Au, and only to aliphatic C–H stretches at ET/Au, confirms the composition of the chain structure at these systems.[16b] Key, however, is the appearance of both types of vibrational features at PES/Au, which, in accord with earlier findings,[6] reveals the presence of both aliphatic and aromatic functionalities at the gold surfaces.

Together, the above findings provide clear evidence for S–C cleavage in monolayers prepared at gold from organosulfides. Preliminary experiments have also shown that S–C cleavage occurs for monolayers formed from longer chain length systems (e.g., dodecyl sulfide). Interestingly, estimates of the relative amounts of each type of adsorbate from the Q_d values in the $i-E$ curve at PES/Au suggest that the preference in bond cleavage reflects, at least in part, the differences in the S–C bond energy[17] at the phenyl (~89 kcal/mol) and ethyl side arms (~74 kcal/mol). Preliminary studies at monolayers of other asymmetric sulfides (e.g., allyl methyl sulfide) follow this prediction. Thermodynamically, S–C cleavage of organosulfides (~74 kcal/mol for BS) is comparable to breakage of a S–H bond in various thiol systems (~87 kcal/mol for BT; ~82 kcal/mol for TP) and is somewhat larger than that at S–S bonds in dialkyl disulfides (~74 kcal/mol for dibutyl disulfide; ~55 kcal/mol for diphenyl disulfide). Therefore, the formation of a gold-bound thiolate from an organosulfide species is thermodynamically consistent with the process operative in the formation of monolayers from alkanethiols and alkyl disulfides.

Studies to detail this newly discovered pathway are underway, focusing in part on byproduct analysis.[18] Perhaps the more interesting and significant questions to be probed are how general is S–C bond cleavage in these systems, what are the broad implications to gold–sulfur binding at sulfur-containing monolayers, and how does this type of reactivity fit in the framework of that observed at other metals.[19]

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(14) The difference in the E_p value at ET/Au relative to TP/Au and PS/Au was attributed previously to the difference in the donor strengths of the ethyl and phenyl substituents on the interaction between sulfur and gold. Additionally, the surface coverage estimated from the Q_d value at TP/Au, and hence at PS/Au, which agrees with that found earlier,[5c] reflects the steric bulk of the phenyl group. Although not yet fully understood, we suspect that the greater estimated coverage at ET/Au relative to BT/Au arises from the roughening of gold in solutions of short chain alkanethiols (see: Sondag-Huethorst, J. A. M.; Schönenberger, C.; Fokkink, L. G. J. *J. Phys. Chem.* **1994**, *98*, 6826–34 and references therein).

(15) The Q_d values under each of the waves were estimated using the general shapes of the curves for the single component monolayers as a basis of an approximate deconvolution.

(16) (a) The S($2p_{3/2}$) peak positions are 162.0 (TP), 162.1 (PS), 162.0 (PES), and 161.9 (ET) eV, with the S($2p_{1/2}$) peak positions ~1.2 eV higher than the corresponding S($2p_{3/2}$) peaks. The shoulder at the lower energy side of the S($2p_{3/2}$) peak is attributed to a trace level of a sulfur/polysulfur species.[9] (b) The aliphatic C–H stretches are at 2970, 2955, 2920, and 2867 cm^{-1} for ET/Au. The aromatic C–H stretch[5a,d] for TP/Au, PS/Au, and PES/Au is at 3063 cm^{-1}.

(17) (a) Oae, S. *Organic Chemistry of Sulfur*; Plenum Press: New York, 1977. (b) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23–35.

(18) C–S cleavage has been observed at nickel catalysts and follows a free radical mechanism (e.g., RSR′ → R–R′; Norman, K.; Meyers, C. Y. *The Chemistry of Organic Sulfur Compounds*; Pergamon Press: Oxford, 1966; Vol. 2, pp 39). It is also known[16a] that when the sulfur atom of an organosulfide donates electrons to an electrophilic reagent, the C–S bond becomes markedly weakened. We believe this situation to be analogous to the events that transpire in monolayer formation at gold. The resulting intermediate ($R-S^{\delta+}-R'$) weakens one of the C–S bonds and leads to C–S cleavage. Our preliminary product assays of the monolayer-forming solutions after sample preparation indicate the presence of higher molecular weight and carbonyl-containing species, the latter suggesting an alternate, but presently unknown reaction pathway.

(19) (a) Scandroff, C. J.; Herschbach, D. R. *J. Phys. Chem.* **1982**, *86*, 3277–9. (b) Ohno, N.; Uehara, J.; Aramaki, K. *J. Electrochem. Soc.* **1993**, *140*, 2512–9.